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# Evolution of Two-Dimensional Structure Phase Transitions $(3 \times 1) \rightarrow (2 \times 1)$ and $(1 \times 1) \rightarrow (2 \times 1)$ on Hydrogen-Terminated Si(100) Surface

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On the Si(100) surface, monohydride dimers (H–Si–H or M–M) and dihydride (H–Si–H or D) species can form an ordered mixture with  $(3 \times 1)$ ,  $(1 \times 1)$  and  $(2 \times 1)$  phases. Thermal annealing at elevated temperatures causes both the  $(3 \times 1)$  and  $(1 \times 1)$  domains to transform to the  $(2 \times 1)$  monohydride phase. We utilize scanning tunneling microscopy to observe these two-dimensional structure phase transitions on the atomic scale. The results show that the coverage of the  $(3 \times 1)$  and  $(1 \times 1)$  domains decays linearly with a common half-life time of ~9.8 h at 570 K. In good agreement with a previous report, this finding suggests that the two different transitions are governed by the same reaction mechanism, i.e., the dihydride-pair recombination mechanism. [DOI: 10.1143/JJAP.45.2197]

KEYWORDS: STM, silicon, hydrogen, desorption, phase transition

#### 1. Introduction

The mechanism and atomistic processes of two-dimensional (2D) structure phase transition are an important subject in fundamental science. With the aid of microscopic techniques such as scanning tunneling microscopy, surface structure can now be observed in real space and at atomic resolution. Thus, phase transitions on surfaces can provide much opportunity for detailed observation and understanding on the 2D phase transitions. One of the most-studied phase transitions on semiconductor surfaces is the H/ Si(100)- $(3 \times 1) \rightarrow H/Si(100)$ - $(2 \times 1)$  transformation.<sup>1)</sup> Hydrogen is the simplest atom and many semiconductor process gases contain hydrogen.<sup>2)</sup> In the processing of silicon surfaces, the role of the formation and destruction of surface Si-H bonds is often dominant in controlling the processes desired. From the fundamental point of view, hydrogenated Si(100) surfaces offer much advantage in theoretical calculation and modeling, and have long been studied as a prototypical system for understanding the dynamics and kinetics of chemisorption and molecular desorption on covalent surfaces with different surface structures.<sup>3-6)</sup>

The Si(100) surface is stabilized by a  $(2 \times 1)$  surface reconstruction, where the atoms of the outermost layer couple in pairs to form Si-Si dimers in order to reduce half the density of dangling bonds (2 per atom) of an ideally bulk-truncated surface. The dangling bonds in the Si(100)- $(2 \times 1)$  surface, one on each dimer atom, are quite reactive toward atoms with unpaired electrons, such as atomic hydrogen. Atomic hydrogen exposure on the clean Si(100)-(2  $\times$  1) surface leads to three known different hydride structures depending on sample temperature and dosage. Most commonly observed is the  $(2 \times 1)$  monohydride structure where Si-Si dimer bonds are preserved.4) These dangling bonds are passivated by hydrogen to produce monohydride dimer H-Si-Si-H (or M-M, where M stands for H–Si). Another structure is the  $(1 \times 1)$  phase, which is often obtained by continuing H-exposure on the  $(2 \times 1)$ monohydride surface near room temperature.<sup>7,8)</sup> Without sufficient thermal excitation, impinging atomic hydrogen simply breaks the dimer bonds in the M–M dimers and subsequently caps the broken (dangling) bonds, forming SiH<sub>2</sub> dihydride (D) species:  $M-M + 2H \rightarrow DD$ . The third structure, (3 × 1), is formed in a narrow temperature range around 400 K.<sup>1,8–10)</sup> The (3 × 1) phase is an ordered mixture of the monohydride dimer and dihydride units, i.e., in units of D(M–M).

The coverage of H on the ideal  $(2 \times 1)$ ,  $(3 \times 1)$  and  $(1 \times 1)$  phases on Si(100) is 1, 4/3 and 2 ML, respectively  $(1 \text{ ML} = 6.8 \times 10^{14} \text{ atoms/cm}^2)$ . Hence, the structure phase transitions between the  $(1 \times 1) \rightarrow (2 \times 1)$  and  $(3 \times 1) \rightarrow$  $(2 \times 1)$  involve the pathways of desorbing surface hydrogen. While atomic H flux is commonly used to surface chemisorption, hydrogen desorbs molecularly. Therefore, the two transitions are mainly governed by the H<sub>2</sub> recombinative desorption from the monohydride and/or dihydride species. Ferng et al. found experimentally that desorption from the  $(1 \times 1)$  dihydride phase involves a pair of neighboring dihydrides linked along the tetrahedral bond direction:  $DD \rightarrow M-M+H_2$ .<sup>11)</sup> The  $(3 \times 1) \rightarrow (2 \times 1)$  transition was first observed at 575 K by low-energy electron diffraction.<sup>12)</sup> Local electron-beam excitation using STM tips was found to induce the creation of local  $(2 \times 1)$  subunits on the  $(3 \times 1)$  phase at room temperature. Energy barriers of various rearrangement pathways of the  $(3 \times 1) \rightarrow (2 \times 1)$ transition following the loss of two H atoms were also calculated on the basis of density function theory.<sup>10)</sup> Because dihydrides in  $(3 \times 1)$  domains are separated in the tetrahedral bond direction by monohydride dimers, the thermally activated  $(3 \times 1)$  to  $(2 \times 1)$  transition is geometrically impossible to occur in a single desorption step from a pair of dihydrides. Ferng et al. found that a position switching of dihydrides with neighboring monohydrides takes place before H<sub>2</sub> desorption.<sup>11)</sup> In this study we shall present more analysis and provide further insight for both phase transitions of H/Si(100)-(3  $\times$  1) and H/Si(100)-(1  $\times$  1)  $\rightarrow$  $H/Si(100)-(2 \times 1).$ 

#### 2. Experimental

Our experiments were performed using a scanning tunneling microscope in an ultra-high-vacuum chamber with a base pressure of  $1 \times 10^{-10}$  Torr. Si(100) samples were mounted on holders made of Ta and Mo. Both the sample

holders and the samples were out-gassed for 12 h at 900 K. The starting clean Si(100)-(2 × 1) surfaces were prepared by brief direct Joule heating at ~1400 K with subsequent radiation quenching. Atomic hydrogen was produced by backfilling the chamber to a background pressure of  $2 \times 10^{-7}$  Torr in the presence of a 1800 K tungsten filament, installed ~5 cm away from the sample. The flux of atomic hydrogen was not measured, and the exposure was recorded in terms of the background dosage of H<sub>2</sub> inside the chamber. An indirect heating stage with a thermal couple is used for the phase transition at 570 K. All images were taken at room temperature in the constant-current mode with a sample bias of +2.3 V.

## 3. Results and Discussion

Following procedures developed previously, a mixed dihydride and monohydride structure is generated by dosing 120 L hydrogen at  $\sim$ 400 K on the H/Si(100)-(2 × 1) surface that was beforehand prepared by dosing 90 L hydrogen on a clean Si(100)- $(2 \times 1)$  surface at 600 K.<sup>12)</sup> As Fig. 1(a) displays, a typical surface so prepared consists of  $(3 \times 1)$ domains (purple) and small areas with  $(2 \times 1)$  (green) and  $(1 \times 1)$  structures. The dark pits, having a depth of about one monolayer, were single or double vacancies depending on their width. The  $3 \times 1$  domains are separated by vacancies and three kinds of characteristic antiphase boundaries, which possess local  $(1 \times 1)$  (labeled I),  $(2 \times 1)$  (labeled II) and  $(3 \times 1)$  (labeled III) order, respectively. In consistence with a previous study,<sup>1)</sup> the local  $(1 \times 1)$  domains consist of no more than two dihydride rows because of the repulsive interaction between dihydride units. Also, vacancy clusters persist on the surface as a result of etching.<sup>1)</sup>

Figures 1(b)–1(d) show STM images of a hydrogenterminated Si(100) surface after annealing at 570 K for 0.5, 4.5, and 33 h, respectively. The annealing temperature is barely above the threshold for desorption.<sup>7,13)</sup> The coverage of various phases as a function of annealing time is displayed in Fig. 2. Although desorption of SiH<sub>4</sub> and SiH<sub>2</sub> molecules as etching products and refilling of desorption sites by mobile surface Si species could have occurred,<sup>14,15)</sup> Figures 1 and 2 show that these effects do not lead to obvious variations in the distribution and density of vacancies within a few percents of statistical uncertainty. Thus, annealing does not significantly induce surface etching; instead, it slowly converts both the (1 × 1) and (3 × 1) phases to (2 × 1) by desorbing hydrogen.

The atomic details of the structure transformation from mixed dihydride and monohydride to the monohydride  $(2 \times 1)$  phases have been reported previously.<sup>11)</sup> Briefly, desorption from dihydrides involves a pair of neighboring dihydrides linked along the tetrahedral bond direction, i.e.,  $DD \rightarrow M-M + H_2$ ; an example is labeled as  $\delta$  in Fig. 3. The same desorption mechanism applies to the  $(3 \times 1)$  domains via first a position switch of dihydrides with neighboring monohydrides, i.e.,  $D(M-M)D(M-M) \rightarrow DD(M-M)(M-M) \rightarrow (M-M)(M-M) + H_2$ ; an example is marked as  $\varepsilon$  in Fig. 3. The switch of adjacent monohydride and dihydride species in a  $(3 \times 1)$  domain results in two dihydride species lying side by side along the Si–H bond directions; examples are labeled as  $\chi$  in Fig. 3. Although several bonds (Si–H and Si–Si) are involved, the energy



Fig. 1. Time evolution of H/Si(100) observed through STM images taken at room temperature after sample was heated at 570 K for (a) 0, (b) 0.5, (c) 4.5, and (d) 33 h. The initial H coverage was about 1.4 ML. The  $(3 \times 1)$  and  $(2 \times 1)$  areas are colored purple and green, respectively, except in (d) for the sake of clarity. The dark pits are single or double vacancies.

barrier of this switching reaction is calculated to be only  $\sim 1.6 \,\text{eV}$ ,<sup>16)</sup> which is in reasonable agreement with that estimated from the reaction temperature of 570 K.

The initial switch ( $\chi$ ) reaction occurs randomly, leading to the random emergence of local (2 × 1) ordering in the (3 × 1) domains, as Fig. 1(b) demonstrates. Figure 3 shows that the transition sites exhibit no notable preference near antiphase boundaries, steps or defects. The switch and the subsequent H<sub>2</sub> desorption in (3 × 1) domains creates local (2 × 1) domains of sizes ( $n \times 8$ ). The (2 × 1) domains of monohydride dimers due to H<sub>2</sub> desorption from the (1 × 1), i.e., (M–M)DD(M–M)  $\rightarrow$  (M–M)(M–M)(M–M) + H<sub>2</sub>, have sizes of ( $n \times 6$ ). The antiphase boundaries of two (3 × 1) domains along the dimer rows' direction, D(M–M) + (M– M)D, consist of two monohydride dimer rows lying side by side and are exhibited as islands of sizes ( $n \times 4$ ). These three



Fig. 2. Coverage for vacancies (triangles),  $(1 \times 1)$  (filled triangles),  $(3 \times 1)$  (filled circles), and  $(2 \times 1)$  (open circles) domains as functions of annealing time at 570 K. The fitting curves for the  $(3 \times 1)$ ,  $(1 \times 1)$  and  $(2 \times 1)$  domains are  $87.4e^{-0.071t}$ ,  $6.8e^{-0.070t}$ , and  $90.5(1 - e^{-0.075t})$ , respectively.



Fig. 3. STM images after nominal H/Si(100)-(3  $\times$  1) surface is annealed at 570 K for 0.5 h. The product of a desorption process from dihydridepair recombination is labeled as  $\delta$ ; of a position switch process,  $\chi$ ; of a desorption process following a position switch,  $\varepsilon$ .

kinds of local  $(2 \times 1)$  domains (green) are dispersed in the  $(3 \times 1)$  domains (purple), as Figs. 1(b) and 1(c) display.

Apparently, the two-step H<sub>2</sub> desorption reactions prefer slightly the ends of  $(2 \times 1)$  dimer rows, causing the  $(2 \times 1)$ domains to extend in the dimer row direction and the  $(3 \times 1)$ domains to shrink, as Figs. 1(c) and 1(d) show. As annealing continues, the  $(2 \times 1)$  areas grow and coalesce into larger domains while new clusters of  $(2 \times 1)$  dimers continue to emerge at the expense of the  $(3 \times 1)$  and  $(1 \times 1)$  domains, as shown in Figs. 1(c) and 1(d). The exponential form of the growth of  $(2 \times 1)$  domains and the decay of  $(3 \times 1)$  and  $(1 \times 1)$  domains suggest an approximately linear growth/ decay behavior. A standard curve fitting gives decay constants of 0.070 and 0.071 or equivalently half-lives of 9.9 and 9.8 h for the  $(1 \times 1)$  and  $(3 \times 1)$  domains, respectively, at 570 K. Since the decay constant is very sensitive to the change in activation energy, the similar decay constants for the two phase transformations strongly suggest that they share a common fundamental and dominant mechanism. As discussed, the  $(1 \times 1) \rightarrow (2 \times 1)$  transition takes place via direct H<sub>2</sub> recombinative desorption from two neighboring dihydrides, while the  $(3 \times 1) \rightarrow (2 \times 1)$  transition requires a switching reaction before the common H<sub>2</sub> desorption from dihydrides. The dominant mechanism is, therefore, the common H<sub>2</sub> desorption, not the switching reaction between a dihydride radical and a monohydride dimer. This conjecture suggests a faster switching mechanism, a slower desorption mechanism, and the existence of the intermediate state. Indeed, the intermediate local  $(1 \times 1)$  phase consisting a DD dihydride pair after the switching reaction (i.e., near

### 4. Conclusions

We have performed real-space measurements on the structure evolution during hydrogen reduction from 1.4 to 1.0 ML on the hydrogen-terminated Si(100) surface with mixed (3 × 1) and (1 × 1) phases at 570 K. Both the initial (3 × 1) and (1 × 1) domains linearly decay with a common half-life time of ~9.8 h. Most H reduction from either the (3 × 1) or (1 × 1) domains involves recombinative desorption of H<sub>2</sub> from two adjacent dihydride (DD) units along the Si–H bond direction. These findings together suggest that the (3 × 1) structure first transforms to the local (1 × 1) structure before the dominant dihydride-pair recombination mechanism occurs.

label  $\chi$ ) is commonly observed in the STM images.

## 5. Acknowledgements

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